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Communications

Formation of $(MgCl_2)_x$ Polynuclear Species During Preparation of Active $MgCl_2$ Supported Ziegler–Natta Catalysts from Solid Solvates with Lewis Bases

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Heterogeneous, highly active, highly isospecific Ziegler–Natta catalytic systems (ZN) consist of solid particles comprising an $MgCl_2$ active support, titanium tetrachloride, and an "internal" electron donor. These catalytic systems have nowadays reached amazing performances, in spite of the intrinsic difficulties in the manipulation and design due to their multisite nature.[1] Significant progress, indeed, has been made in understanding the catalyst chemistry, i.e., how the activity, stereoselectivity, hydrogen response of these systems can be finely tuned, through the choice of the internal donor, generally coupled with the use of an external donor. This has been accomplished through careful control of the catalyst architecture, a fundamental step to achieving the fine-tuning of the polymer morphology directly from the reactor plants. According to this modern technology, olefin-based homo and copolymers, which exhibit the best combination of fluidity, stiffness, and impact resistance, may be obtained, so that a wide range of application areas is covered.[1]

A typical process for the preparation of supports with improved controlled morphology and outstanding performances consists of the precipitation of $MgCl_2 \cdot n$ETOH complexes, with ETOH = ethanol and $n \approx 2$–3, from oil/molten complex emulsions by rapid cooling.[1] This process produces spherical particles with a narrow size distribution, whose reaction with $TiCl_4$ and other catalyst components creates active forms of $MgCl_2$ with a high degree of porosity, which are used in Ziegler–Natta catalysis. The nature of these active forms and the origin of the high degree of nanoporosity of these catalysts is still unclear. The high porosity, in turn, seems to play a key role in determining the so-called "replica" effect. This effect consists of the retaining of the spherical morphology of the catalysts in the polymer through suitable prepolymerization treatments.[1a]

Regardless of the nature of the Lewis base (LB), $MgCl_2 \cdot n$LB complexes with $n = 2$–3 are generally crystalline, and characterized by the presence of polymeric $(MgCl_2)_x$ chains of the kind shown in structures A and B of Figure 1.[2a,b] In all cases, at the end of the process, the base content becomes very low ($n < 0.3$) and the final catalyst essentially consists of the disordered δ form of $MgCl_2$.[2c] In this active form of $MgCl_2$, consecutive Cl−Mg−Cl sandwich layers (Figure 2A) are disorderly stacked along c according to a hexagonal or cubic sequence or rotated by ± 60° each other.[3a] The X-ray powder diffraction profiles of the δ form

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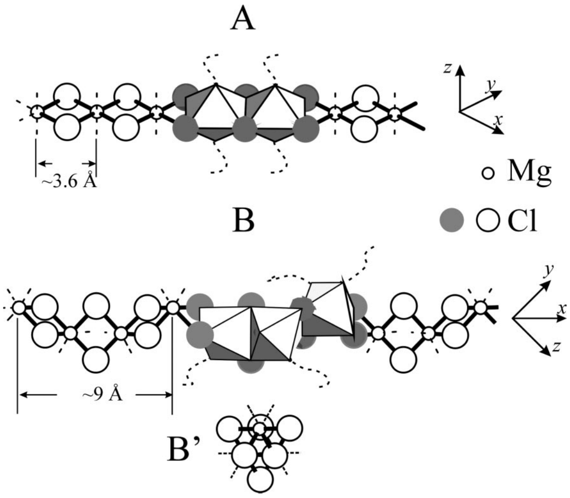

Figure 1. Structural models of the $(MgCl_2)_x$ polymer chains that characterize the crystal structures of the complexes (A) $MgCl_2 \cdot 2.5(CH_3COOC_2H_5)$[2a] and (B) $MgCl_2 \cdot 2(HCOOC_2H_5)$[2b]. In these chains, the Mg atoms are bridged by chlorine atoms while keeping an octahedral coordination geometry, and couples of first neighboring octahedra share edges. (A) Linear chain with identity period of 3.6 Å and (B,B′) 3_1 helix with identity period of 9 Å in projections parallel (B) and perpendicular (B′) to the chain axis. The coordination sites around Mg atoms occupied by a Lewis base molecule are indicated with dashed lines. The octahedral coordination of Mg atoms is indicated by the shadowed polyhedra.

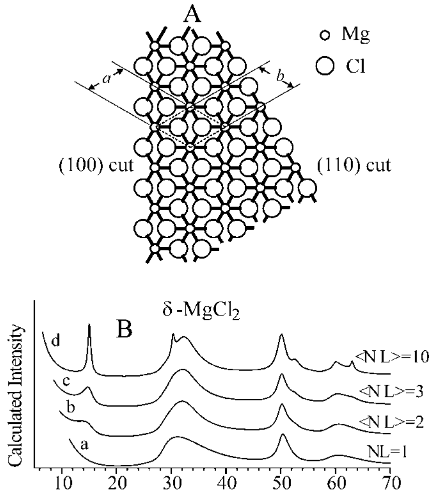

Figure 2. (A) Model of Cl−Mg−Cl structural layer in $MgCl_2$ layer compounds showing the (100) and (110) cuts. The hexagonal unit-cell parameters $a = b = 3.64$ Å are also indicated.[3] (B) Calculated X-ray diffraction profiles for the δ modification of $MgCl_2$, corresponding to a completely statistical sequence of structural layers A along the normal to the layers (c-axis) and the indicated numbers of structural layers piled along the c-axis (NL).

of $MgCl_2$ show two diffraction peaks centered at 2θ (Cu Kα) ≈ 15° ($d = 5.90$ Å) and $2\theta \approx 50°$ ($d = 1.82$ Å), and a broad asymmetric halo in the 2θ range 30−35° (Figure 2B).

In this communication, we report a study of the nature of the active forms of $MgCl_2$ and show that they basically correspond to δ $MgCl_2$. Moreover, we show that the high degree of porosity of the supported catalysts obtained starting from $MgCl_2 \cdot n$LB solid solvates with $n = 2$–3, responsible for the high activity of the supported ZN catalysts, may be due to structural transformations, which produce amorphous or highly disordered crystalline $MgCl_2$ polynuclear species. These species are characterized by a chainlike structure, reminiscent of the polymeric $[MgCl_2 \cdot n\text{LB}]_x$ chains, which characterize the crystal structure of the starting adducts.

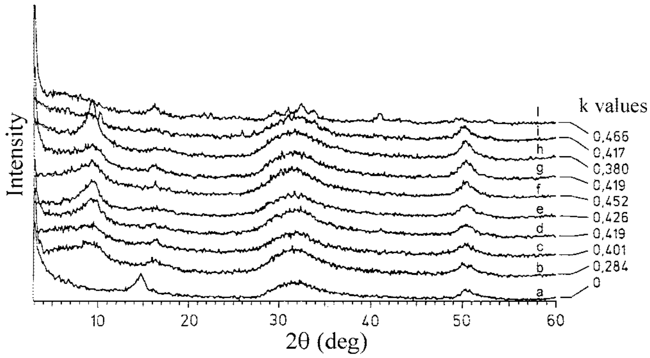

Figure 3. X-ray powder diffraction profiles (Ni-filtered Cu Kα radiation) of $[MgCl_2(HCOOC_2H_5)_k(TiCl_4)_m]_x$ titanated adduct for $0 \leq k < 0.5$ and $m/k \approx 0.16$, redrawn from ref 2c.

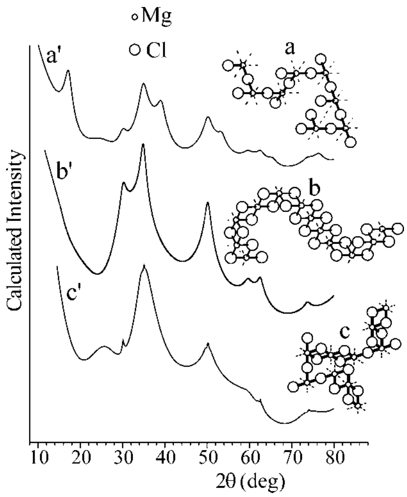

Figure 4. Structural models of $(MgCl_2)_x$ polynuclear species with consecutive octahedra sharing (a) corners, (b) edges, and (c) edges and corners, and corresponding calculated X-ray diffraction profiles. These disordered successions of $MgCl_2$ units give rise, in the long term, to a three-dimensional network.

The typical X-ray diffraction profiles obtained at low base content from the $MgCl_2 \cdot n$LB solid solvates by addition of $TiCl_4$ are reported in Figure 3, redrawn from ref 2c. These diffraction profiles show the typical diffraction features of δ-$MgCl_2$ (Figure 2B). Extra reflections at $2\theta \approx 10$, 30, 32, 35, 38, 40, and 48° are also present, along with a large amount of diffuse scattering (curves b−l of Figure 3). It is apparent that the intensities of the diffraction peaks typical of δ-$MgCl_2$ increase, whereas those of the extra reflections progressively decrease with decreasing base content.

To unravel the origin of these extra reflections, we have calculated the X-ray diffraction patterns of some structural models of polynuclear $(MgCl_2)_x$ species in which magnesium atoms are bridged exclusively by chlorine atoms while keeping an octahedral coordination geometry and considering that couples of first neighboring octahedra may share corners and/or edges (Figure 4a−c). The disordered successions of $(MgCl_2)$ units of the kind shown in Figure 4a−c give rise in the long term to a three-dimensional network. The calculated X-ray diffraction profiles of the disordered chainlike arrays of ($MgCl_2$) units shown in Figure 4a−c are presented in Figure 4a′-c′.

The most remarkable result of the present calculations is that the calculated X-ray diffraction patterns from disordered arrays of ($MgCl_2$) units, forming a three-dimensional network, may present Bragg reflections (for instance, the profile of Figure 4b′ with diffraction peaks at $2\theta \approx 30$, 35, 50, 59, and 63°) in addition to a large amount of diffuse scattering, despite the high degree of structural disorder. The position and intensity of these reflections are close to those of the spurious diffraction peaks present in the X-ray diffraction profiles of $MgCl_2 \cdot n$LB solid solvates upon addition of $TiCl_4$, at low base content (curves b−l of Figure 3).

We suggest that these amorphous structures play a key role in the crystallization of the active δ form of $MgCl_2$ starting from the solid complex solvates used in the industrial preparation of heterogeneous Ziegler–Natta catalysts. The three-dimensional network structure of these disordered species, indeed, may explain the high degree of nanoporosity of these catalysts. Since the Ti catalytic sites are supposed to be located at the edge of thin δ-$MgCl_2$ lamellae,[1,4] a high degree of nanoporosity increases the contour length of the lateral faces of $MgCl_2$ crystals available for the epitactic coordination of titanium species and of internal and external donor molecules (Figure 2A). Therefore, an accurate manipulation of the initial $MgCl_2 \cdot n$LB adducts of suitable initial stochiometry plays a key role in the formation of nanoporous δ-$MgCl_2$ crystals, through the formation of intermediate chainlike $(MgCl_2)_x$ amorphous species having a three-dimensional network structure in equilibrium with the active δ-form of $MgCl_2$.

The most important microscopic parameter that is affected by the processing conditions of the Ziegler–Natta catalysts, indeed, is the concentration of Mg sites available for the coordination of active species, which, in turn, depends on the size, concentration, and distribution of nanopores.[1] Our analysis suggests that a deep understanding of the structural transformations that occur during the late stages of the catalysts preparation may be highly beneficial not only in fundamental studies of the Ziegler–Natta stereospecific polymerization of olefins but also in practical application because it allows for a better optimization of the processing conditions for obtainment of nanoporous δ-$MgCl_2$ crystals.

Acknowledgment. The paper is dedicated to the memory of Paolo Corradini, who gave fundamental contributions in understanding the mechanism of stereospecific Ziegler–Natta polymerization of olefins.

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